

CLAIMS

1. A substrate, at least one part of the surface of which has been rendered hydrophobic, having for this purpose a hydrophobic surface structure comprising an essentially mineral silicon-containing sublayer and an outer layer of hydrophobic agent grafted onto said sublayer, characterized in that said sublayer has received the outer layer of hydrophobic agent although it had a surface that was in an activated state before being brought into contact with said hydrophobic agent.
2. The substrate as claimed in claim 1, characterized in that the sublayer is a hard sublayer.
3. The substrate as claimed in either of claims 1 and 2, characterized in that it is formed by a plate, whether plane or with curved faces, of monolithic or laminated glass, of glass-ceramic or of a hard thermoplastic, such as polycarbonate.
4. The substrate as claimed in claim 3, characterized in that the sublayer of the hydrophobic coating forms part of the substrate, the latter being formed by a plate, whether plane or with curved faces, of monolithic or laminated glass or of glass-ceramic, the composition of which, at least on the surface, corresponds to that of the essentially mineral silicon-containing sublayer.
5. The substrate as claimed in claim 4, characterized in that the substrate is a glass dealkalized at least on its surface.
6. The substrate as claimed in one of claims 1 to 5, characterized in that said sublayer is formed by a compound chosen from  $\text{SiO}_x$ , where  $x \leq 2$ ,  $\text{SiOC}$ ,  $\text{SiON}$ ,  $\text{SiOCN}$  and  $\text{Si}_3\text{N}_4$ , it being possible for hydrogen to be

combined in all proportions with  $\text{SiO}_x$ , where  $x \leq 2$ ,  
SiOC, SiON and SiOCN.

7. The substrate as claimed in one of claims 1 to 6,  
5 characterized in that the silicon-containing sublayer  
contains aluminum, in particular up to 8% by weight, or  
carbon, Ti, Zr, Zn and B.

8. The substrate as claimed in one of claims 1 to 7,  
10 characterized in that the silicon-containing sublayer  
when its surface is in the activated state has a  
thickness of between 20 nm and 250 nm, especially  
between 30 nm and 100 nm and in particular between  
30 nm and 75 nm.

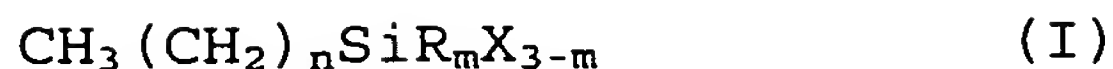
15 9. The substrate as claimed in one of claims 1 to 8,  
characterized in that the silicon-containing sublayer  
has, when its surface is in the activated state, an RMS  
roughness of between 0.1 nm and 40 nm, in particular  
20 between a few nm and 30 nm.

10. The substrate as claimed in one of claims 1 to 9,  
characterized in that the silicon-containing sublayer  
when its surface is in the activated state has an  
25 actual developed area at least 40% greater than the  
initial plane area.

11. The substrate as claimed in one of claims 1 to 10,  
characterized in that the silicon-containing sublayer  
30 when its surface is in the activated state has a  
hardness such that it does not delaminate after 100  
revolutions, and preferably up to 200 revolutions, in  
the Taber test.

35 12. The substrate as claimed in one of claims 1 to 11,  
characterized in that the outer layer of hydrophobic  
agent is based on a hydrophobic agent chosen from:

(a) alkylsilanes of formula (I):

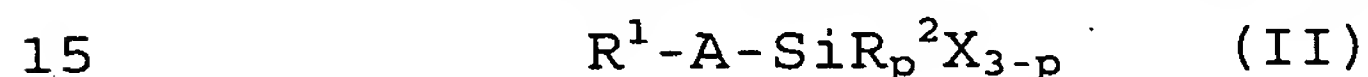


in which:

- n ranges from 0 to 30, more particularly from 0 to 18;
- 5      - m = 0, 1, 2 or 3;
- R represents an optionally functionalized organic chain; and
- X represents a hydrolyzable residue, such as an  $\text{OR}^0$  residue, where  $\text{R}^0$  represents hydrogen; or a  
10      linear, branched or cyclic, especially  $\text{C}_1\text{-C}_8$ , alkyl residue; or an aryl residue; or such as a halo, for example chloro, residue;

(b) compounds with grafted silicone chains;

(c) fluorosilanes, such as those of formula (II):



in which:

- $\text{R}^1$  represents an especially  $\text{C}_1\text{-C}_9$  monofluoroalkyl, oligofluoroalkyl or  
perfluoroalkyl residue; or a monoaryl, oligoaryl  
20      or perfluoroaryl residue;
- A represents a hydrocarbon chain, optionally interrupted by a heteroatom such as O or S;
- $\text{R}^2$  represents a linear, branched or cyclic, especially  $\text{C}_1\text{-C}_8$ , alkyl residue, or an aryl  
25      residue; X represents a hydrolyzable residue, such as an  $\text{OR}^3$  residue, where  $\text{R}^3$  represents hydrogen or a linear, branched or cyclic, especially  $\text{C}_1\text{-C}_8$ , alkyl residue; or an aryl residue; or such as a halo, for example chloro, residue; and
- 30      - p = 0, 1 or 2.

13. The substrate as claimed in one of claims 1 to 12, characterized in that the layer of hydrophobic agent has a thickness of between 1 and 100 nm, preferably  
35      between 2 and 50 nm.

14. The substrate as claimed in one of claims 1 to 13, characterized in that the layer of hydrophobic agent

has a weight per unit area of grafted fluorine of between  $0.1 \mu\text{g}/\text{cm}^2$  and  $3.5 \mu\text{g}/\text{cm}^2$ .

15. A process for manufacturing a substrate as defined  
5 in one of claims 1 to 14, characterized in that a coating layer of hydrophobic agent is deposited, in at least one pass, on the surface of a silicon-containing mineral layer formed at least partly on the surface of the substrate, said deposition of the hydrophobic agent  
10 taking place while said surface is in the activated state.

16. The process as claimed in claim 15, characterized in that an activated surface of the silicon-containing  
15 mineral layer is obtained by depositing it under conditions in which its surface is obtained directly in the activated state.

17. The process as claimed in claim 15, characterized  
20 in that an activated surface of the silicon-containing mineral layer is obtained by carrying out an activation treatment in at least one pass.

18. The process as claimed in one of claims 15 to 17,  
25 characterized in that the hydrophobic agent is deposited within the shortest possible time, preferably between 1 second and 15 minutes, after the activated surface has been obtained.

30 19. The process as claimed in either of claims 17 and 18, characterized in that an activation treatment is carried out under conditions that do not go as far as etching, by the use of a plasma or an ionized gas, at reduced or atmospheric pressure, chosen from air,  
35 oxygen, nitrogen, argon, hydrogen, ammonia and mixtures thereof, or by the use of an ion beam.

20. The process as claimed in either of claims 17 and

18, characterized in that an activation treatment is carried out under conditions that allow a silicon-containing layer to be etched, by the use of a plasma of at least one fluorine-containing gas chosen from SF<sub>6</sub>,  
5 CF<sub>4</sub>, C<sub>2</sub>F<sub>6</sub> and other fluorinated gases, where appropriate combined with oxygen, it being possible for the oxygen to represent up to 50% by volume of the etching plasma.

21. The process as claimed in claim 20, characterized  
10 in that the activation carried out under conditions that allow the silicon-containing layer to be etched by an activation treatment, which does not cause additional etching but does still modify the chemical nature and/or the electrostatic state of said layer, is  
15 monitored.

22. The process as claimed in one of claims 15 to 21, characterized in that the silicon-containing layer is deposited, cold, on the substrate by vacuum cathode  
20 sputtering, preferably magnetron sputtering and/or ion beam sputtering, or by low-pressure or atmospheric-pressure PECVD (plasma-enhanced chemical vapor deposition), or else deposited hot by pyrolysis.

25 23. The process as claimed in claim 22, characterized in that a layer of SiO<sub>2</sub> is deposited, as silicon-containing layer, by PECVD, using a mixture of an organic or nonorganic, silicon-containing precursor, such as SiH<sub>4</sub>, hexamethyldisiloxane, tetraethoxysilane  
30 and tetramethyldisiloxane, and an oxidizer, the subsequent activation being carried out in the same chamber or in a separate chamber.

24. The process as claimed in one of claims 15 to 23,  
35 characterized in that the fluorosilane layer is deposited by wiping-on, evaporation or spraying of a solution containing the fluorosilane, or by dipping, spin-coating, flow-coating, etc., using a solution

containing the fluorosilane.

25. The process as claimed in one of claims 15 to 24  
for the manufacture of glazing having a hydrophobic  
5 coating, characterized in that the sublayer is  
deposited on the glass on a glass manufacturing line  
using the "float" process while the glass is being  
supported by the bath of molten tin, or in a subsequent  
step, that is to say on leaving the bath of molten tin,  
10 in that the conversion operations are then carried out,  
such as bending, toughening and/or assembling,  
especially by lamination, in order to obtain plates of  
glass made up from one or more sheets coated with the  
sublayer on at least one face, in that the sublayer or  
15 sublayers supported by said plates are then activated  
and in that, finally, a functionalization by the  
hydrophobic agent of the sublayer or sublayers thus  
activated is carried out.

20 26. The process as claimed in one of claims 15 to 24  
for the manufacture of glazing having a hydrophobic  
coating, characterized in that sheets of glass are  
manufactured by the float process, in that said glass  
sheets are then converted by operations such as  
25 bending, toughening and/or assembling, especially  
lamination, in order to obtain plates of glass made up  
from one or more sheets, in that the sublayer is then  
deposited on at least one face of the plates thus  
obtained, and in that the sublayer or sublayers are  
30 then activated, followed by the functionalization by  
the hydrophobic agent of the sublayer or sublayers thus  
activated.

27. The process as claimed in one of claims 15 to 24,  
35 characterized in that the sublayer is deposited on at  
least one face of glass sheets obtained upon leaving  
the float process, in that these sheets thus coated  
with the sublayer or sublayers are converted, limiting

the techniques used to those that do not damage said sublayer(s), and in that the sublayer or sublayers are then activated, followed by the functionalization by the hydrophobic agent of said sublayer or sublayers  
5 thus activated.

28. Rain-repellent glazing comprising a substrate as defined in one of claims 1 to 14 or manufactured by the process as defined in one of claims 15 to 27.  
10

29. An application of the glazing as defined in claim 28 as glazing for the automotive, aviation, building, electrical household appliance and ophthalmic lens industries.  
15